Fabrication and Characterization of ZnO Thin Film Based p-n Junctions

(Thesis submitted in partial fulfilment of requirement for the degree of

Integrated Master of Science)

By

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May 2015

Acknowledgement

First I would like to thank my guide Dr. Jyoti Prakash kar for accepting me as project research student and giving me opportunity to learn and work in his "Electronic material and Device fabrication" laboratory. He is very supportive during two years of my research work. He has given me lots of opportunity to learn and innovate, one of which was "Design and Manufacturing of manual probing station for material characterization" for our Lab. I would also like to thank research scholars Mr. Surya Prakash Ghosh, Mr. Kailash Chandra Das and Mr. Nilakantha Tripathy for helping me throughout this project work. I am very grateful to Mr. S.P. Ghosh for teaching me intricacies of sample handling and maintenance. Especially I would like to thank Mr. N. Tripathy for teaching me the details of taking I-V and C-V measurements for characterization of synthesized thin film. Also I would like to l thank my friends Agnish and Rabi for being so nice to me and making my research period enjoying and special.

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Certificate

This is to certify that the two year project entitled "**Fabrication and characterization of ZnO thin film based p-n junctions**" is a record of original research work carried out by **Sandeep Kumar** under my supervision and guidance for partial fulfilment of the requirement of the degree of **Integrated Master of Science** in the department Physics and Astronomy, National Institute of Technology, Rourkela.

Place: **Dr. Jyoti Prakash Kar**

Date: Department of Physics and Astronomy,

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Abstract

Zinc Oxide (ZnO) thin films have drawn considerable interest due to its excellent material properties such as wide and direct band gap, high electron mobility and large exciton binding energy. In order to realise the applications of these devices, fabrication of high quality p-type ZnO thin films are very essential. In this work p-ZnO/n-ZnO and p-ZnO/n-Si type of junctions were realised by depositing the (Al, N) doped p-ZnO films on glass and silicon substrate using low cost sol gel as well as dip coating techniques. The characterization of deposited thin films was carried out by XRD, UV visible spectroscopy, and I-V measurements. For qualitative confirmation for p-type conduction of deposited ZnO thin film hot probe method is utilised. A comparative study of the different p-n junctions was done, where homo-junction between p-ZnO (dip coated) and n-ZnO(sputtered) shows a better diode characterises.

CONTENTS

CHAPTER 1

1. Introduction

In the past 10 years, electronic sensors and optoelectronic devices based on semiconductors have attracted considerable attention due to wide range applications in our daily life. Nowadays, every electronic gadget like photovoltaic cell, organic sensors in medical field, defence system robotics, smart vehicles, cell phones and many more are equipped with advanced electronic devices with quick response and high performance. For making low cost electronic devices ZnO is one of the most promising semiconductors which can be utilised in semiconductor sensor and optoelectronic devices technologies.

For fabricating cheap devices we need low cost semiconducting material like ZnO with accurate electronic property. The major challenge is to find or synthesize p-type semiconductor material for fabrication of p-n junction sensing devices with already existing n-type ZnO semiconductor material.

1.1 Properties of ZnO

Zinc oxide crystallizes in two main structures (1) Hexagonal wurtzite (2) cubic zincblend. The wurtzite structure is most stable at ambient conditions and thus most common. In both cases, the zinc and oxide centers are tetrahedral, the most characteristic geometry for Zn (II). Fig.1.1 represents hexagonal wurtzite structure of Zinc Oxide.

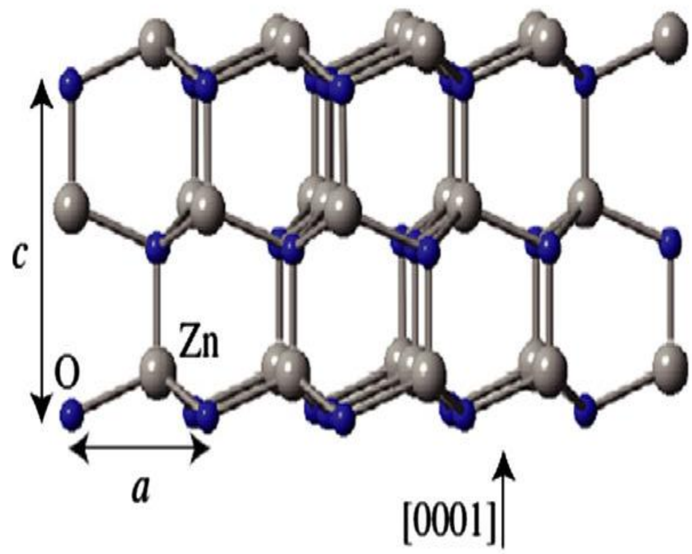

Fig.1.1 Hexagonal wurtzite crystal structure of ZnO

The lattice constants are a = 3.25 Å and c = 5.2 Å; their ratio c/a ~ 1.60 is close to the ideal value for hexagonal cell c/a = 1.633. As in most group II-IV materials, the bonding in ZnO is largely ionic (Zn^{2+}– O^{2-}) with the corresponding radii of 0.074 nm for Zn^{2+} and 0.140 nm for O^{2-}. This property accounts for the preferential formation of wurtzite rather than zinc blend structure [1].

ZnO has gained lots of attention due to it's broad range of interesting properties like

- Wide band gap semi-conductor (3.4 eV).
- High exciton binding energy of 60 meV at room temperature, which is higher than GaN (24 meV)
- Range of conductivity from metallic to insulating
- Room temperature ferromagnetism
- High transparency
- Huge chemical sensing effect
- Become p-type after suitable doping
- Low cost semiconductor material
- Naturally wurtzite ZnO has intrinsically stable n-type semiconducting property.
- High electron mobility.

Since n-type ZnO material is already available due to it's intrinsic nature. Therefore, to realise semiconducting device applications, the major challenge is to investigate suitable p-type materials which can form stable p-n junction with n-type ZnO. The two possible solutions to realise this fabrication are as follows:

Method 1: Preparation of p-type ZnO by using suitable doping such as Nitrogen and other group -V & IV elements.

Method 2: Use of materials such as ZnSe, which is stable to form wurtzite p-type semiconducting material by doping nitrogen.

In Method 1 it is difficult to prepare stable p-type ZnO material due to self-compensation from native donor in ZnO. In Method 2, the main problem needs to be tackled is effect of band gap discontinuities and different material parameters. Some research groups have shown that with dual doping method the p-type characteristic can be obtained for longer time, which indicated more stable material [1].

This project work is focused on synthesis of p-type ZnO using co-doping sol-gel method and fabrication of homogeneous p-n junction with natural ZnO. (Method 1)

1.2 Literature Review

1.2.1 Intrinsic N-Type Behaviour of Natural ZnO

Zhang et al. [2] in their research described n-type behaviour for ZnO by native defects due to following conditions:

- Donors (V_o, Zn_i, Zn_o) have shallow energy levels, so that they readily reproduce electron
- Donors have low formation enthalpy $\bigtriangledown$H, even if E_f is high in the gap, so that the donors become abundant.
- Electron-killer centres (O_i, V_{Zn}) have high formation enthalpy even if E_f is high in the gap, so that they do not form which is approximately true for Zn-rich but not for O-rich conditions.

Therefore intrinsic n-type in ZnO is due to Zn_i in Zn rich condition, which is in good agreement with experimental results [1].

1.2.2 Selection of p-Type dopant and Co-Doping

Research work led by J.C. Fan et al. provided a comprehensive review on p-type materials [1]. They have outlined that co-doping is an effective method to prepare p-type ZnO. This review presents the critical progress of science and technology of p-type ZnO materials. This research review outlined various important issues that need further investigation for transition of ZnO to commercial use. These are following:

- The realization of p-type ZnO materials with higher hole concentration, higher mobility, and lower resistivity.
- Better understanding of the mechanism of p-type doping in ZnO which can help to realise higher p-type doping level in ZnO.
- Bandgap engineering in p-type ZnO is very important for some optoelectronic devices. Therefore, further investigation about modulation of bandgap by doping MgO, BeO, or CdO in p-type ZnO is necessary to develop practical ZnO based devices.

- The achievement of high quality p-n junction based on p-type ZnO is very important to realise high quality and low cost electronic devices.

Li Duan et al. have investigated Silver-Nitrogen doped p-type ZnO by growing films on glass substrate by sol-gel technique [3]. They investigated the influence of dual doping on electrical, structural, and optical properties of the prepared sample. Their research findings showed that the p-type conductivity of dual doped ZnO: (Ag, N) film was stable for longer time rather than mono-doped ZnO films. The resistivity of dual doped ZnO: (Ag, N) was found to be lower than mono-doped ZnO: Ag and ZnO: N. Also p-n junction characteristics were also investigated by fabrication homo-junction of ZnO: (Ag, N) and un-doped ZnO using current-voltage characteristics. This demonstrated a typical stable p-n junction characteristic. Hence this approach is expected as a promising candidate for producing stable p-type ZnO with Dual doping method.

M. Dutta and D. Basak [4], investigated the electrical properties of undoped ZnO and doped ZnO: (Al, N) using Hall measurement. The undoped film showed n-type conductivity. The doped film showed p-type conductivity because of acceptor nature of Aluminium and Nitrogen impurities. They achieved p-ZnO/n-Si hetero-junction by depositing Al-N doped p-type ZnO film on n-type Silicon using a very low cost sol-gel technique. The junction was found to possess good diode characteristic. They also studied the photo-response properties of the hetero-junction by studying the I-V characteristic under ultraviolet (370 nm) and visible light (450 nm) illuminations. The experimental finding of their research suggests that if the quality can be controlled then the sol-gel derived p-type ZnO film is an effective way for low cost junction fabrication.

To produce shallow level of defects, there are two rules for choosing p-type dopants

- The dopants should favor the growth conditions which can suppress the formation of compensation defects, because the solubility of dopants and concentration of intrinsic defect sare depended on the growth conditions.

- Dopants at cation sites in compound semiconductors generally produce shallower acceptor levels than dopants at anion sites. Dopant-substituting cations can cause smaller perturbation in valence-band maximum than dopants at anion sites. For group-I impurities, the valence band maximum state mainly consists of the anion p orbitals with small mixing of the cation p and d orbitals, and then replacing Zn by group-I impurities lead to small perturbations at valence band maximum. Therefore, group-I elements as p type dopant in ZnO have shallower acceptor level compared to the group-V elements.

- Hole-killer centers (V_o, Zn_i, Zn_o) must have high formation enthalpy.

1.2.3 Co-Doping Method

To synthesize high conducting p-type ZnO the co-doping method was suggested by various researchers [5-10]. They considered that acceptor (A) and donor (D) as co-dopants in ratio of A: D=2:1 enhanced the incorporation of acceptor, which lowered the acceptor level and raised the donor levels with the formation of acceptor-donor-acceptor complexes. This kind of complex formation is caused by the strong interaction between acceptor and reactive donor codopants. Fig.1.2.3 represents energy level diagram of dopants in co-doped system.

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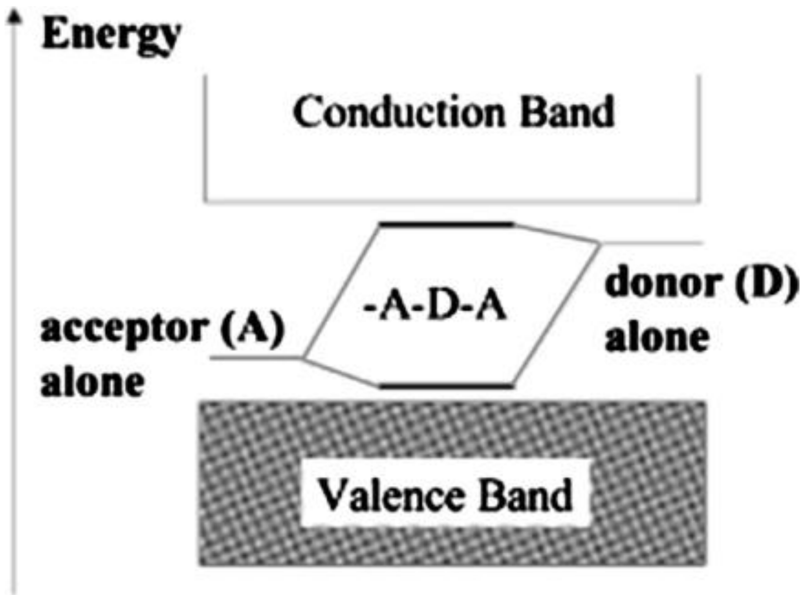


Fig.1.2.3 The schematic energy diagram for p-type co-doped semiconductor [10].

1.2.4 Sol-Gel Technique for Preparation of P-Type ZnO Material

Sol-gel (Chemical solution deposition) technique is a wet chemical technique widely popular in material synthesis. In this method the synthesis starts from a precursor solution which undergoes succession of transformations during its preparation to sol-gel. These transformations in succession are-

(i) Hydrolysis of molecular precursor
(ii) Polymerization via successive bimolecular addition of ions
(iii) Condensation by dehydration
(iv) Nucleation
(v) Growth

Fig.1.2.4 shows main steps of fabrication of thin films and materials by sol gel technique:

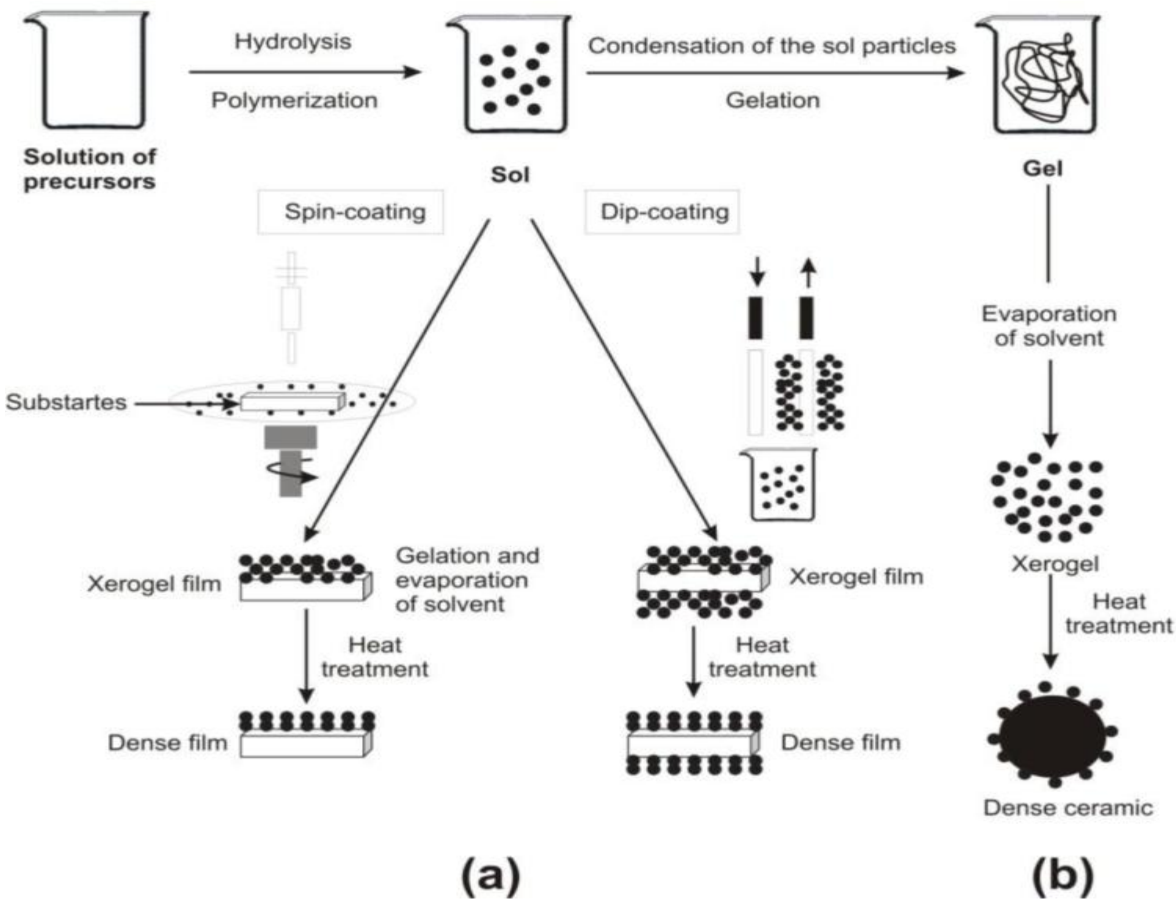


Fig.1.2.4 Overview of fabrication of thin film by sol-gel method (a) Films from a colloidal sol. (b) powder from colloidal solution [1]

CHAPTER 2

2. Design and Manufacturing of Probe-Station

Probe-station is a mechanical device used to physically acquire electronic signals from internal nodes of a semiconductor device and the signal acquired is sent to current-voltage measurement system for its characterization. Probe-station uses manipulator which allows precise positioning of thin needles on the surface of semiconductor device.

Micro Probing stations play very important role in fabrication Industries and scientific research of following areas like Nano-electronics, Magnetism & Spintronics, Organic & Molecular electronics, Semiconductors, Optoelectronics, Micro-electro mechanical systems, Thin film research, Sensor development, Ferroelectrics etc.

In our lab (Electronic Materials & Devices Lab.), mainly IV and CV measurements of semiconductors and dielectric materials are carried out.

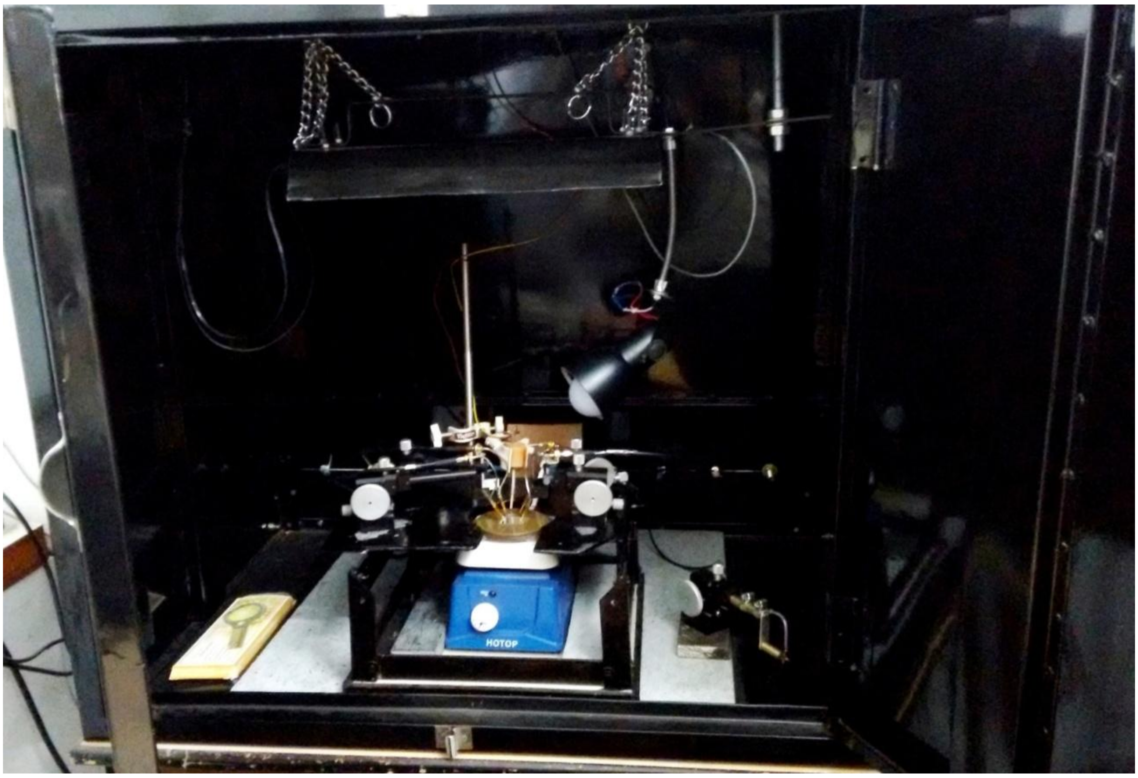


Fig.2.1 Image of I-V and C-V measurement system

Stepwise Process of Manufacturing

Step I. **Cutting metallic angles at corners with precise position and dimensions and drilling holes in metal angles at precise positions according to drawn Fig.2.2**

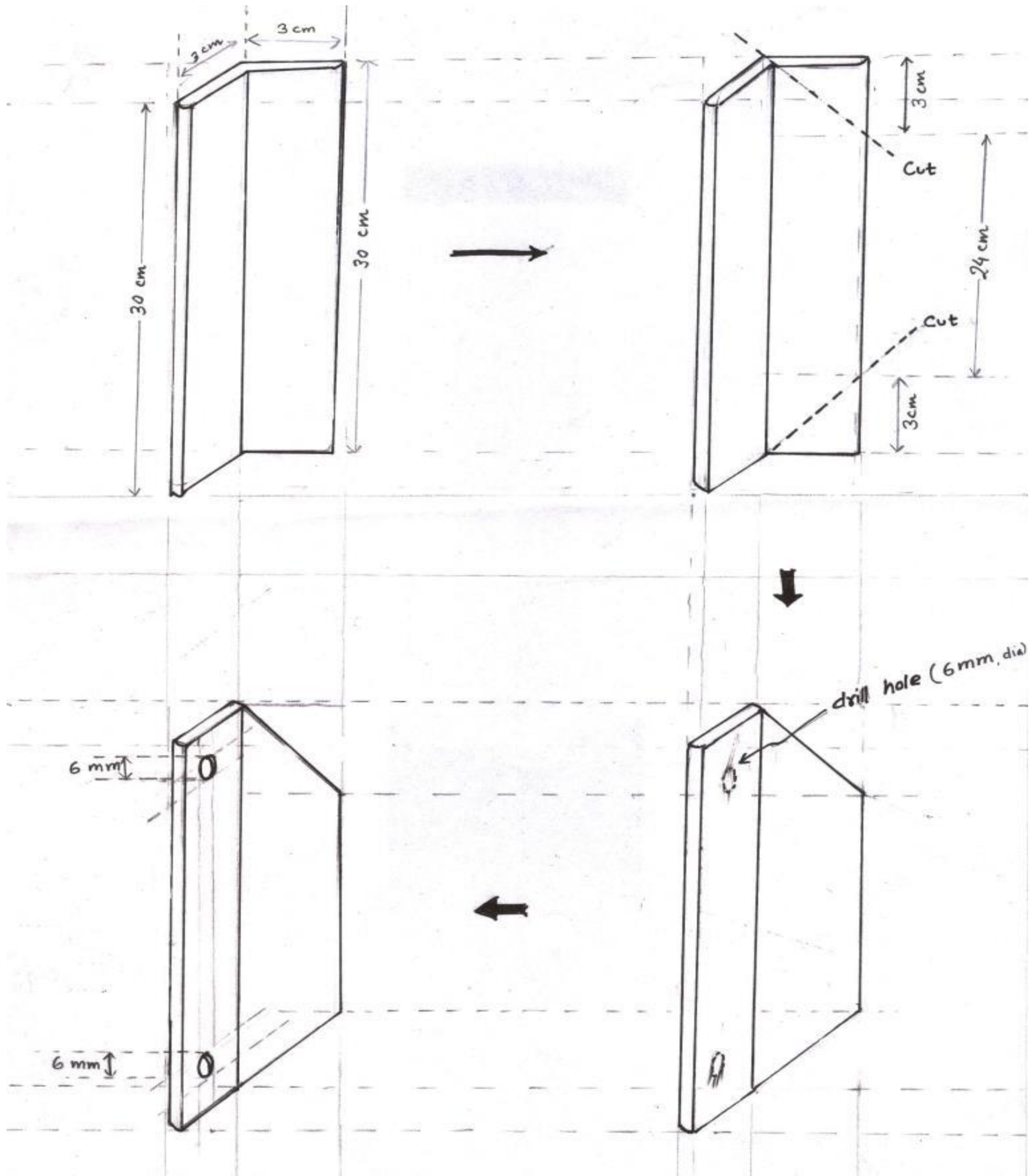


Fig.2.2 Manufacturing of one metal angle for base; four of these are required to form rectangular base.

<u>Step II.</u> Fitting of four metal angles of step 1 together using nuts and bolts to form the base of the probe station according to Fig.2.3

A wooden base is fitted as base below the obtained basic

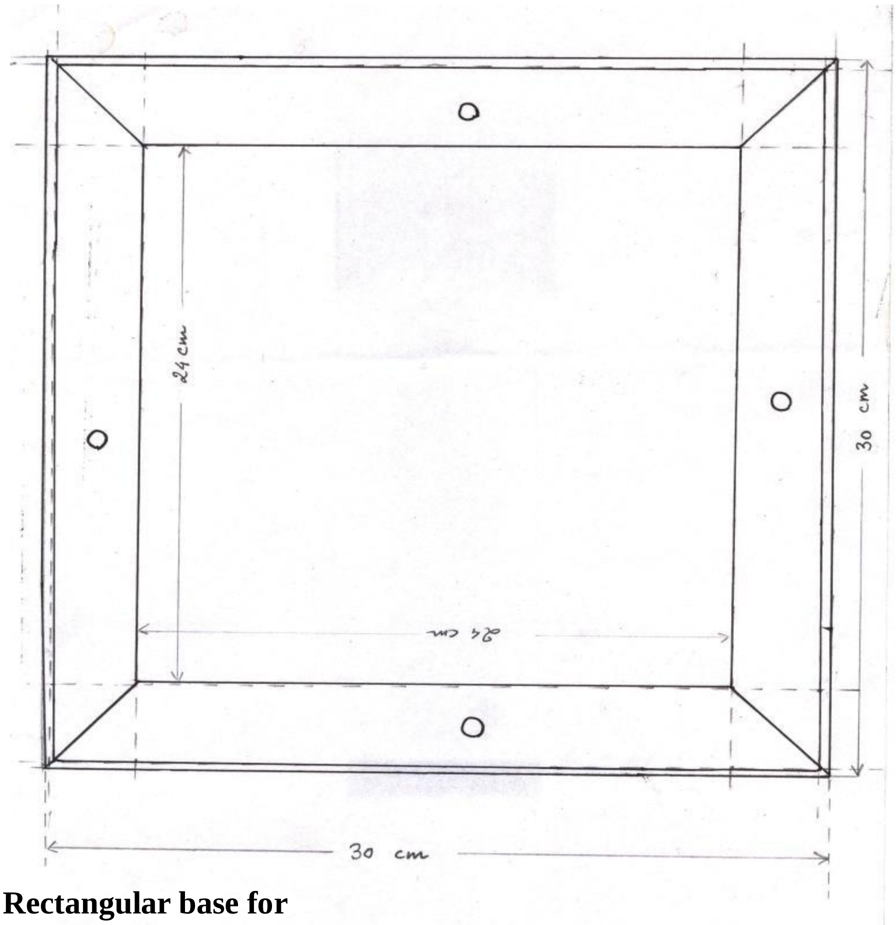


Fig.2.3 Rectangular base for probe-station

<u>Step III</u>. Manufacturing of legs

Four Metal angles of proper dimensions were cut and holes were drilled according to Fig.2.4

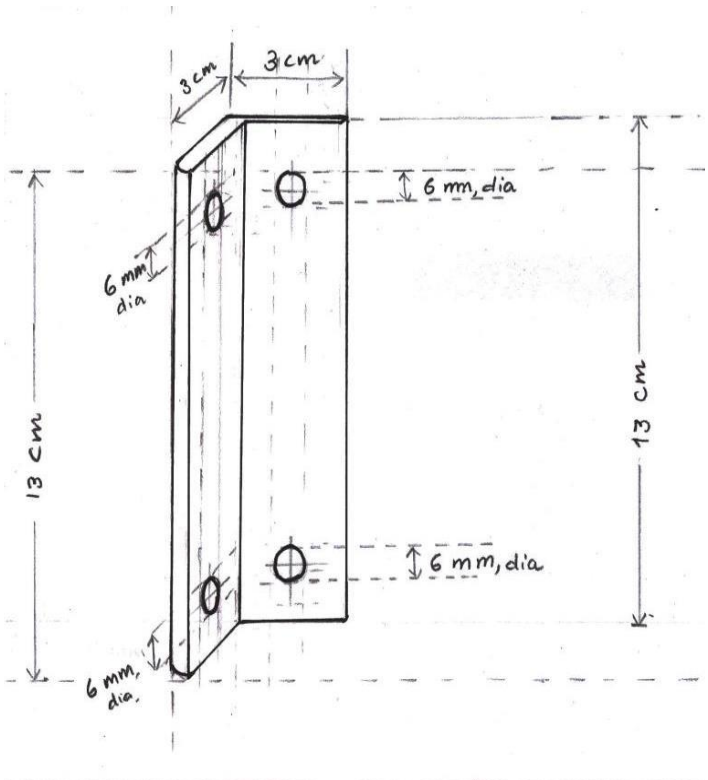


Fig.2.4 One leg of four

Step IV. **Assembling legs with base**

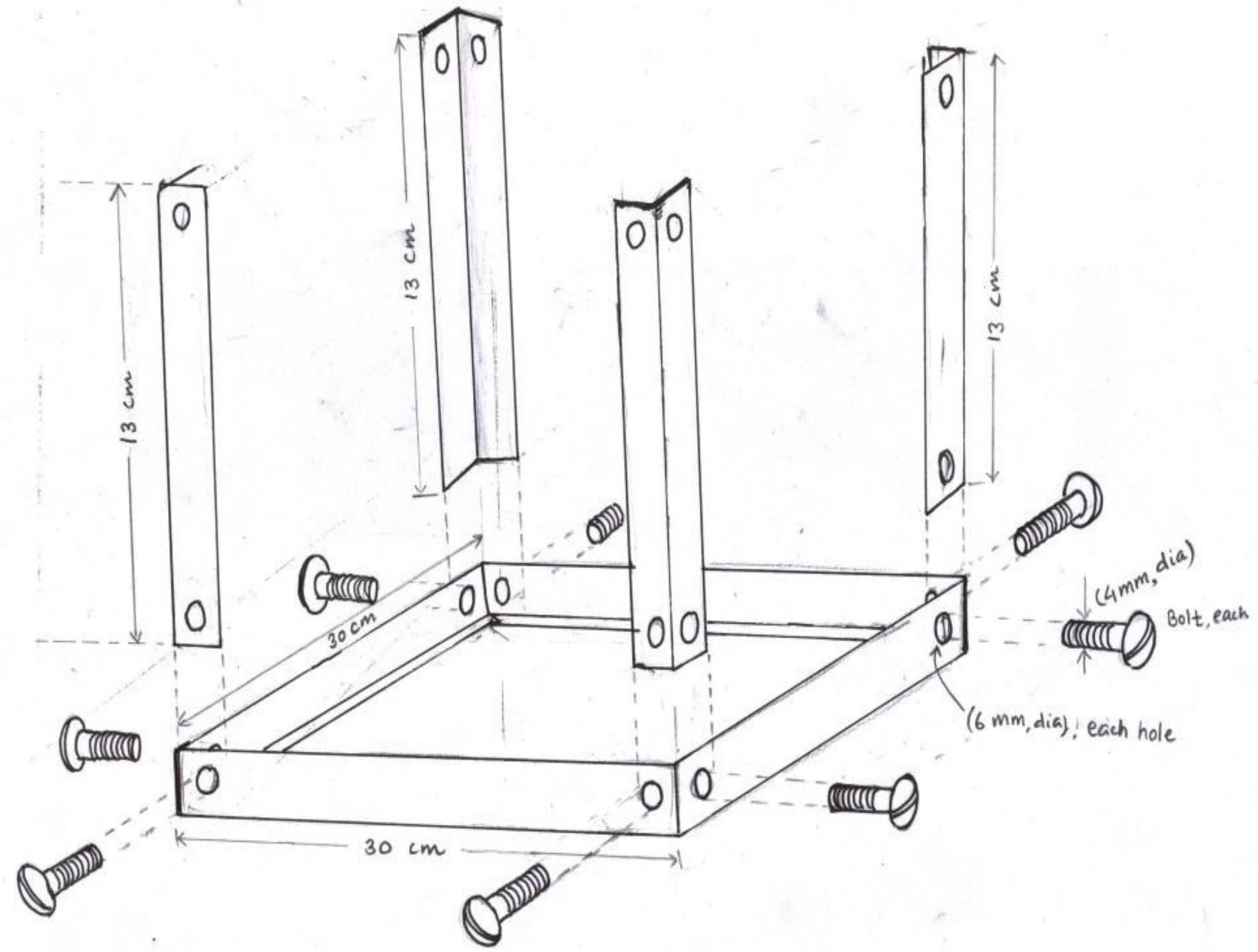
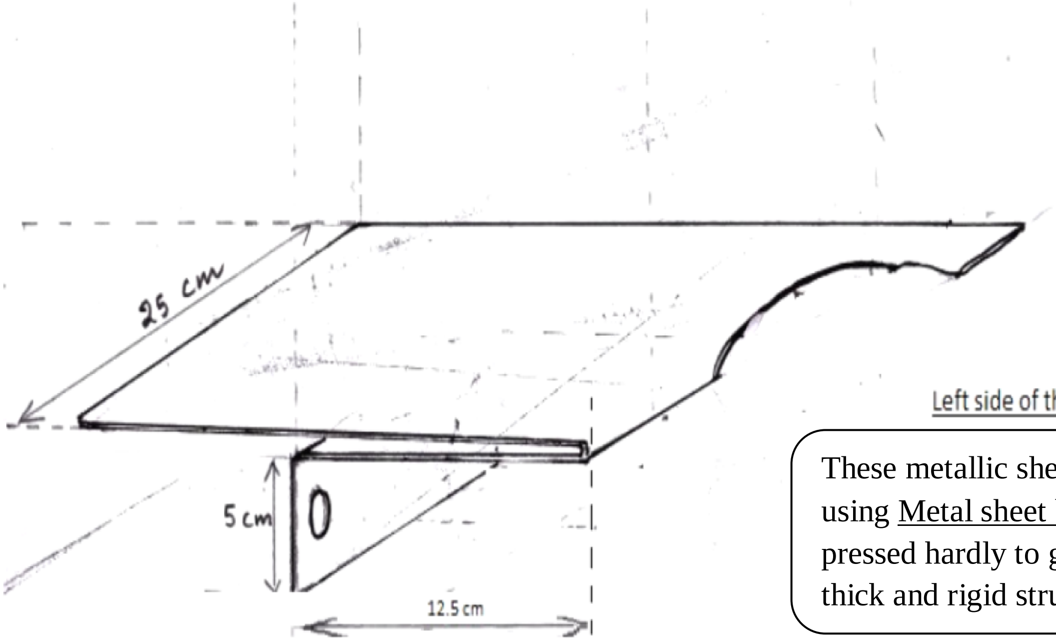


Fig.2.5 Assembly of legs with base; Four legs constructed in step III are fitted with base using nut-bolts of 4mm diameter to form cuboid structure of probe-station

Step V. **Design & Manufacturing of Platen**

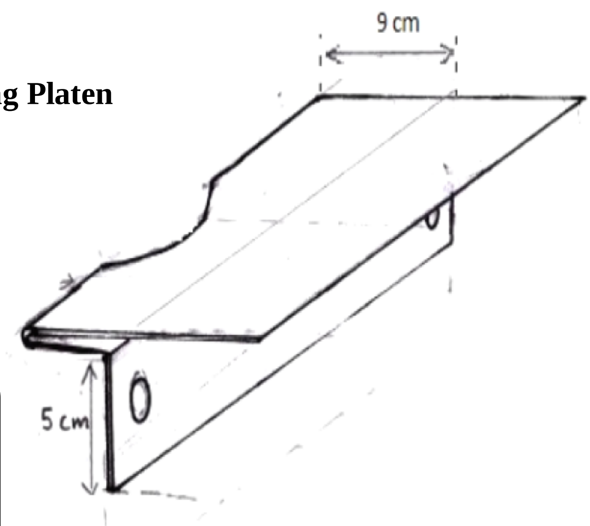


Left side of the platen

These metallic sheets were folded using Metal sheet bender Machine and pressed hardly to give the platen a thick and rigid structure.

A polished and painted thick iron metal sheet of dimension 36cm X 25cm is used to manufacture the left side of the platen of the probing station

Fig.2.6 Sketch representing Platen



Right side of the Platen

A polished and painted thick iron metal sheet of dimension 25cm X 25cm is used to manufacture the right side of the platen of the probing station

Semicircular metallic parts were removed by cutting from both sides of folded metallic sheets to give circular spacing so that chuck could fitted inside and operated from the top of the platen.

<u>Step VI</u>. Assembling of platen on cuboid structure of step IV according to Fig.2.7

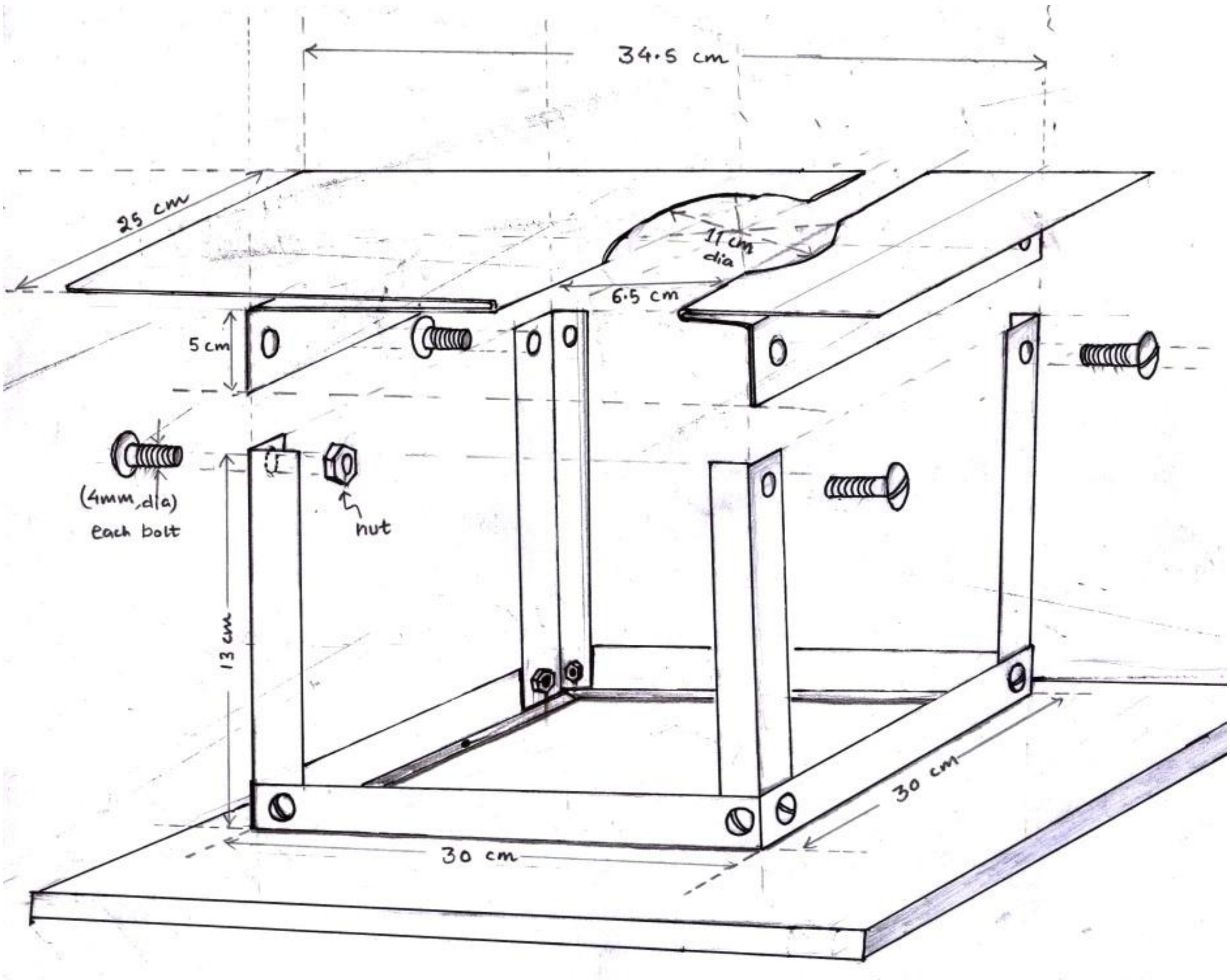


Fig.2.7 Sketch representing assembly of platen on cuboid base

<u>Step VII</u>. Hot plate of appropriate size and copper Chuck (mounted with cooling supply) is assembled inside the cuboid structure obtained in step VI.

Fig.2.8 represents front view of the finally assembled probe station.

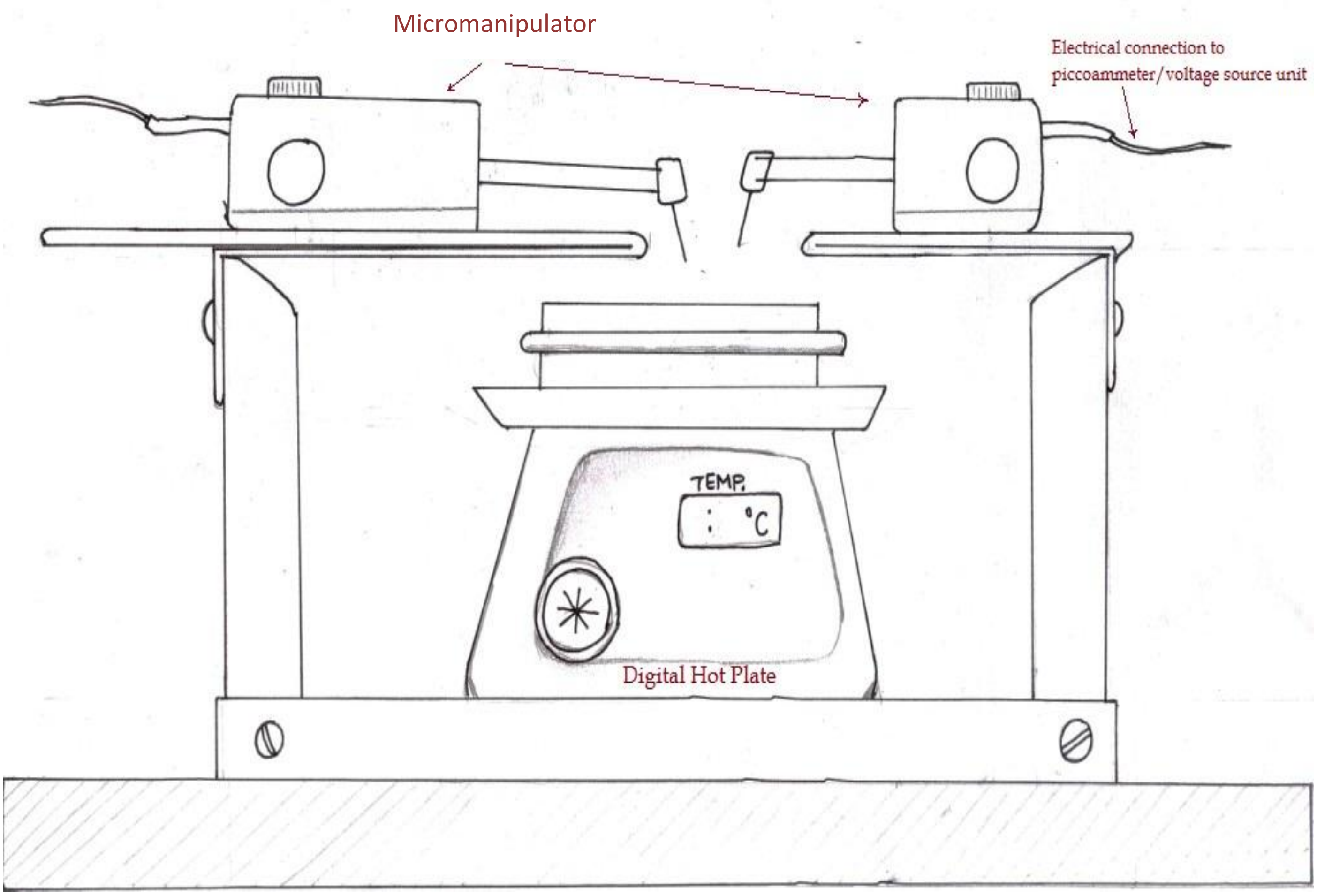


Fig.2.8 Front view of the assembled micromanipulator system

<u>Step VIII.</u> Four micro-probers on metallic stage (platen) are assembled and their electrical connections are made to picoammeter/voltage source [Fig.2.9, Fig.2.10]

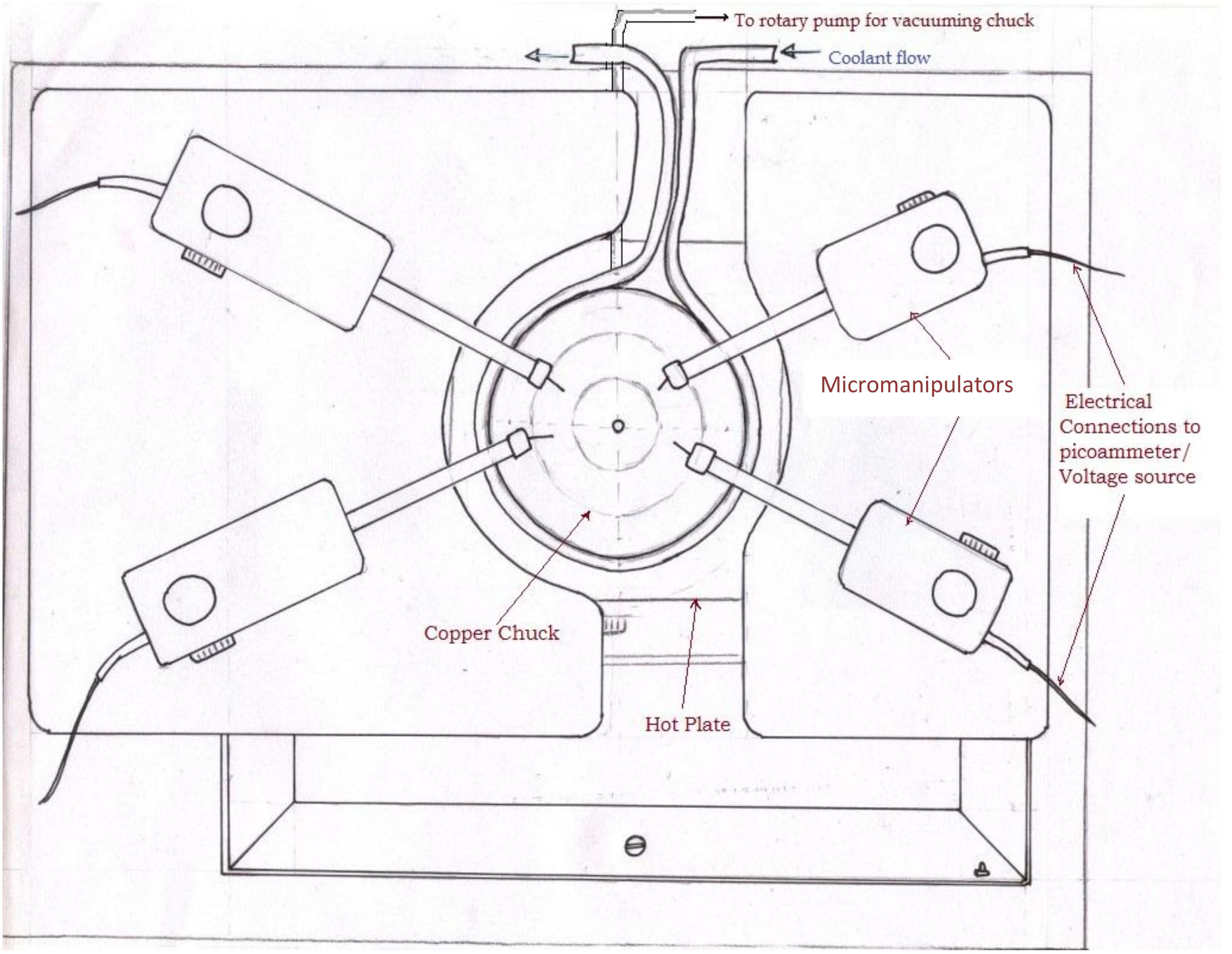


Fig.2.9 Top view of the micromanipulator system

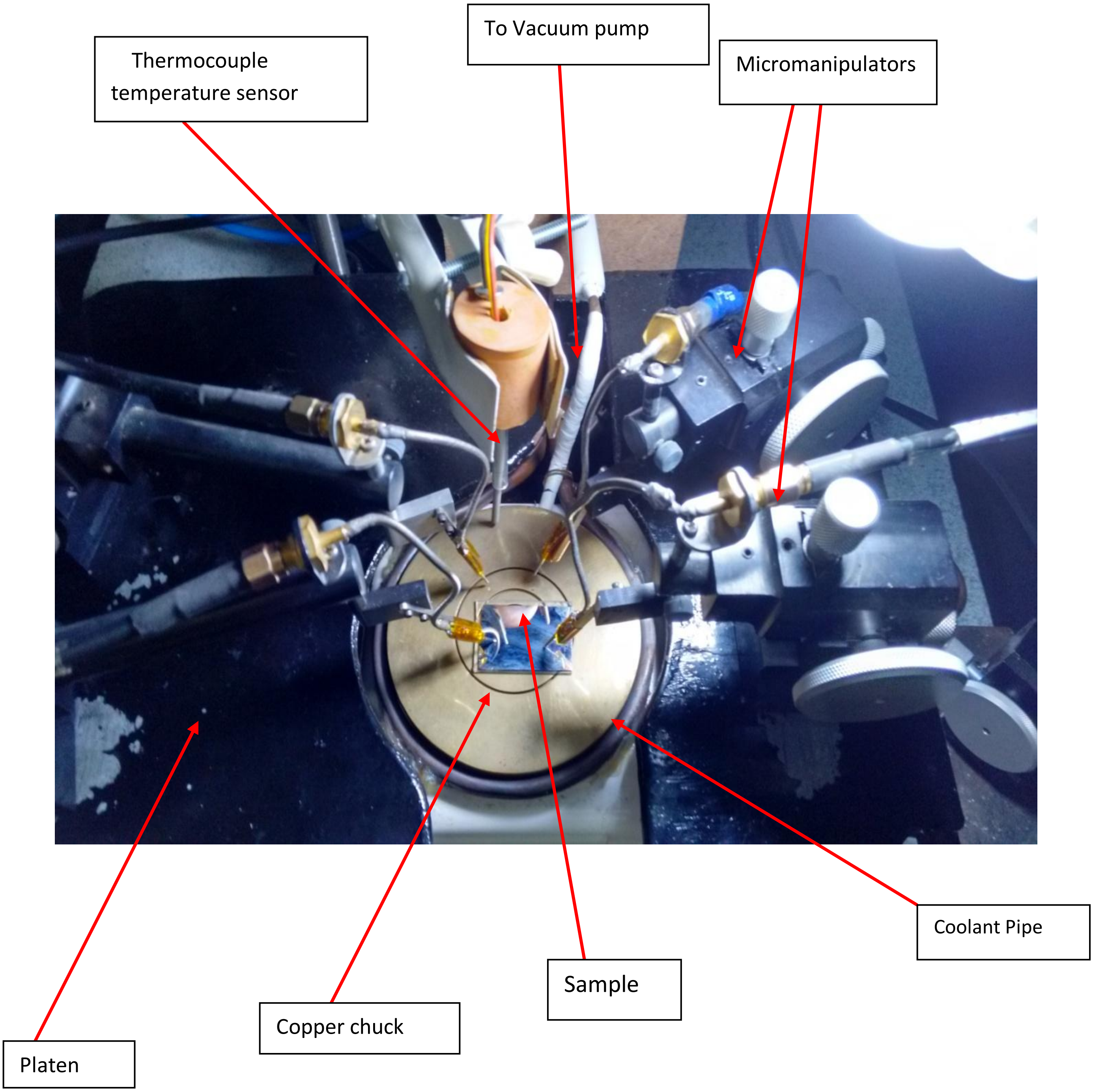


Fig.2.10 Image of the micro-probing station; the complete setup

CHAPTER 3

3. Materials And Methods

3.1 Materials

The chemical method has several advantages like low cost, low temperature, large growth area. Therefore in this study ZnO films were deposited by wet chemical method. For the purpose of comparison another growth technique (sputtering) was also conducted.

3.1.1 Preparation of precursor solution

For synthesis of precursor solution for p-type zno, 0.4 M Solution was prepared by zinc acetate 2-hydrate [$Zn(CH3COOH)_2.2H_2O$] and ethanol as solvent. Aluminium nitrate [$Al(NO3)_3.9H_2O$] and Ammonium acetate [CH_3COONH_4], as aluminium and nitrogen sources, were added to the sol and stirred for 4 hours at 60 C. The atomic ratio of Zn/Al/N was 1:0.01:1. Then 2 ml ethanolamine solution as stabilizer is added to the solution and stirred for 2 hours at 60 C. Ageing of solution was done for more than 24 hrs. All chemicals used in this synthesis are of purity 99 %. Calculated amounts of required chemicals for 0.4 M precursor solution are - zinc acetate dehydrate = 4.39 g, volume of ethanol = 50 ml, volume of ethanolamine (stabiliser) = 2 ml, ammonium acetate = 1.54 g, aluminium nitrate nona hydrate =0.075 g.

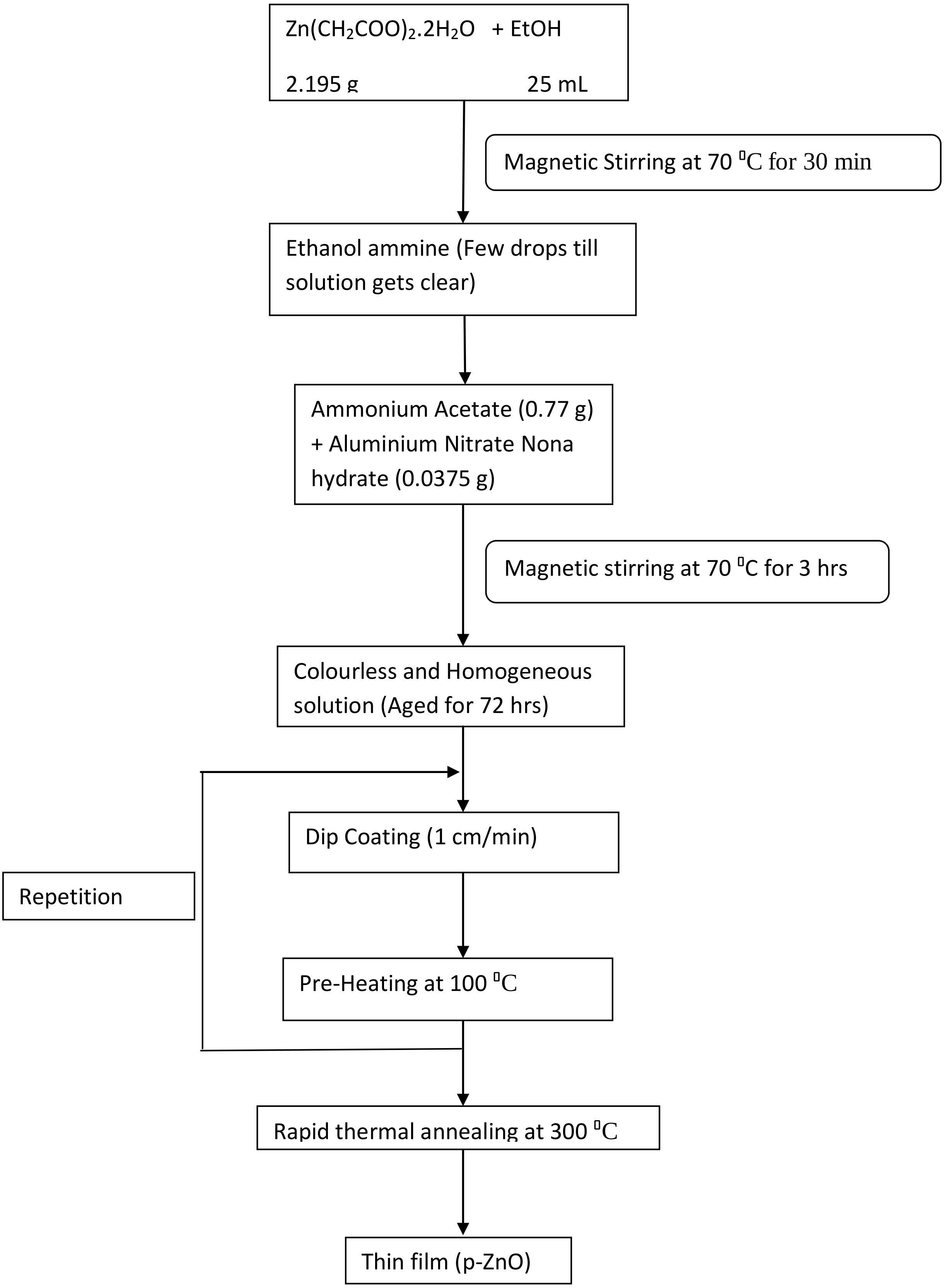


Fig.3.1.1 Block diagram representing sol-gel technique for fabrication of p-type ZnO thin film

3.1.2 Substrate Cleaning

3.2.1.1 Glass Substrate

Following steps of cleaning are used for cleaning of glass substrates-

1. Cleaning of glass substrate with soap and normal water.
2. Sonication of glass slides in acetone with zig for 10 min.
3. Rinsed with de-ionized (DI) water.
4. Sonication of glass slides in isopropyl alcohol (IPA) for 10 min. & finally
5. Sonication of glass slides in de ionized water for 10 min.

3.2.1.2 Silicon Substrate

The steps involved in silicon substrate cleaning are –

1. Sonication of silicon slides (substrates) with zig in acetone for 5 min.
2. Sonication of substrates in DI water for 5 min.
3. Sonication of substrates in IPA-1 for 5 min.
4. Sonication of substrates in IPA-2 for 5 min.
5. Sonication of substrates in IPA-3 for 5 min.
6. Sonication of substrates in DI water for 5 min.
7. Dipped the substrates with zig in beaker filled with H_2SO_4. Added H_2O_2 in 1:1 ratio and left for 10-15 min.
8. Rinsed the substrates with DI water for 5 min.
9. Rinsed the substrates with 5% HF solution.
10. Rinsed with DI water for 5 min.
11. Rinsed again with another beaker of DI water for 5 min.
12. Drying of substrates.

3.1.3 Device structure and fabrication for p-n junction formation [Fig.3.1.3]

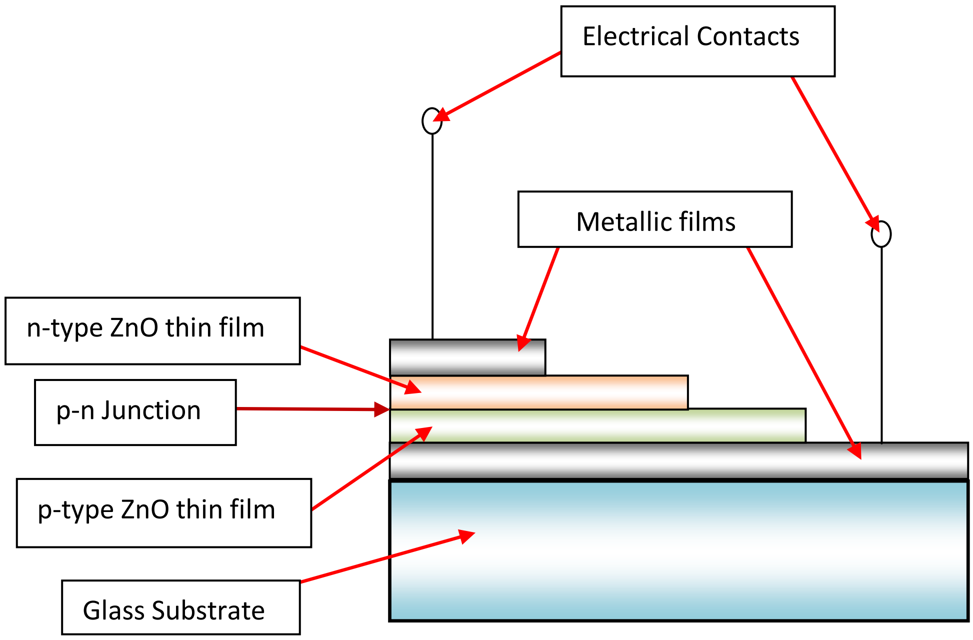


Fig.3.1.3 Schematic diagram of p-n junction formation and characterisation

3.2 CHARACTERIZATION TECHNIQUES

3.2.1 XRD (X-ray diffraction)

XRD technique provides the basic information about crystal structure of the system. This characterisation includes verification of crystalline phase and composition, calculation of miller indices, and crystallinity (amorphous or crystalline). In this characterization technique X-rays are made to incident on the sample. X-rays satisfying the Bragg's condition gets diffracted from the sample. Intensity of diffracted X-ray is plotted with respect to scattering angle. This technique has been used to study change in crystal structures in various experimental conditions like distortion in XRD pattern due to doping.

In this work XRD analysis of thin films have been carried out to verify ZnO peaks and this is compared with co-doped ZnO: (Al, N) film.

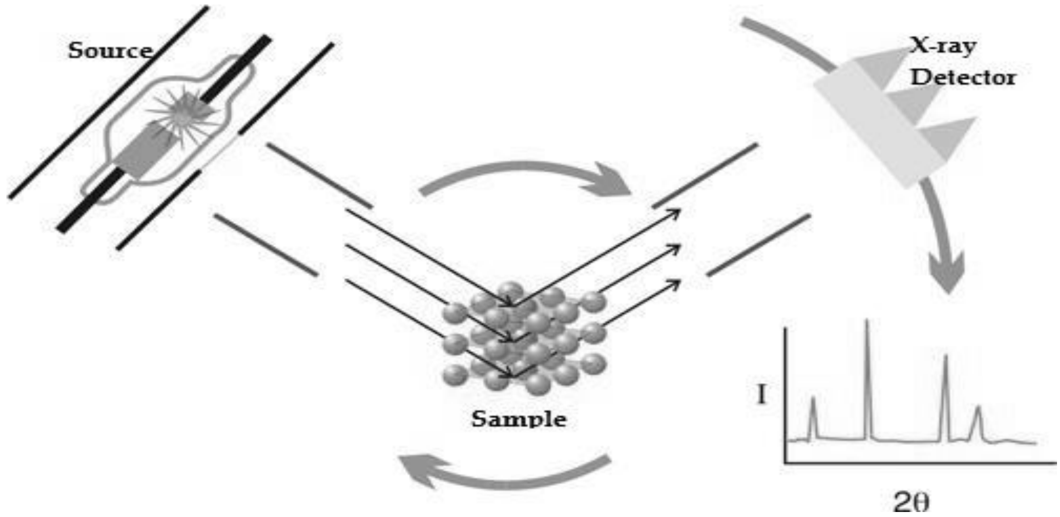


Fig.3.2.1 Schematic diagram of XRD characterization technique

3.2.2 UV- VISIBLE SPECTROSCOPY

UV-visible spectroscopy is a characterisation technique which utilizes electromagnetic waves ranging from ultraviolet to visible to study absorbance, transmittance and reflectance of the material under study. UV-visible spectroscopy is generally used for determination of band gap of the materials. Here, in this project work this technique is used to find band gap of semiconductor ZnO thin film.

Following relation is used for calculation Band Gap of a semiconductor using UV-Visible spectroscopy:

$$(\alpha h\nu)^{\frac{1}{n}} = \mathrm{B}(\mathrm{h}\nu - \mathrm{Eg})$$

α = Absorption Coefficient $= -\log(T/d)$; T = Transmittance; d = Thickness of the film

n = 2; Indirect band Gap, n= ½; Direct Band Gap; B = Constant related to transition probability

3.2.3 Hot Probe Method

It is a very simple method for qualitative determination of type of semiconductor material either of type (p or n) of using digital multimeter and a hot probe attached to COM terminal of the multimeter [Fig.3.2.3]. In this method when two probes of multimeter, set for voltage reading, of which one is hot are touched on semiconductor surface then there is potential gradient generated. The sign of generated potential depends upon the type of material used. If material under examination is p-type semiconductor then the multimeter shows a positive reading of potential difference and if it is n-type then the reading comes with a negative sign.

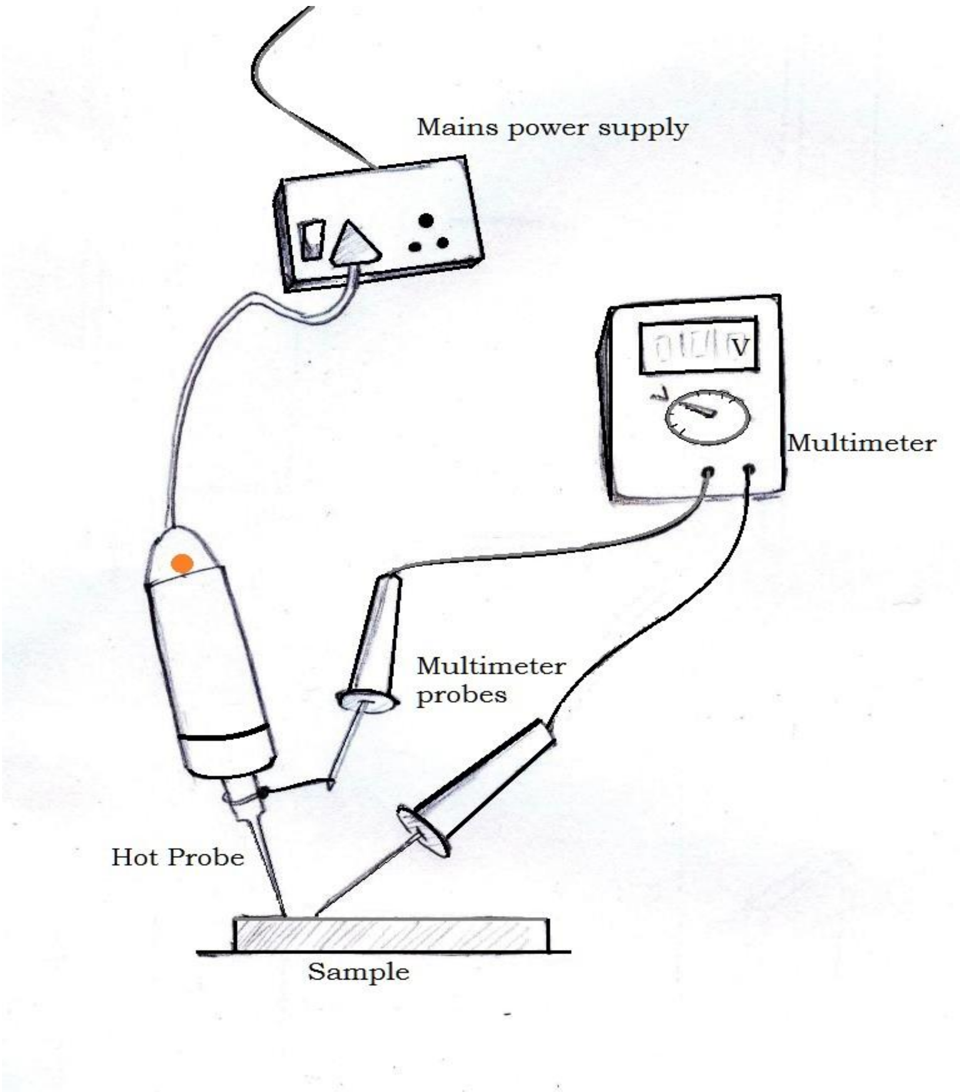


Fig.3.2.3 Schematic diagram representing hot probe method

Semiconductor Sample	Voltage
n-Type	−Ve
p-Type	+Ve

3.2.4 I-V Measurement

A current-voltage (I-V) measurement is used for p-n junction characterization and confirmation of Homo/Hetero junctions between two semiconductor materials. I-V measurements are carried out by making metallic contacts on two sides of junction. During this project work the I-V measurement instrument KEITHLEY picoammeter/voltage source 6487 is used [Fig.3.2.4].

Fig.3.2.4 Image of picoammeter/voltage Source, Electronic Material and Devices Lab. Dept. of Physics & Astronomy

3.3 Thin Film Deposition Techniques

3.3.1 Spin Coating

Spin coating is a very simple and efficient technique for nano-scale thin film deposition on flat surfaces by spinning the substrate at high speed. For deposition of material as thin film, small amount of precursor solution is dropped at centre of the substrate and rotated at high speed using spin coater machine [Fig.3.3.1.1]. The precursor solution then spreads uniformly on the substrate under action of centrifugal force. This method is effectively used in research for micro fabrication of oxide layers using sol-gel precursors.

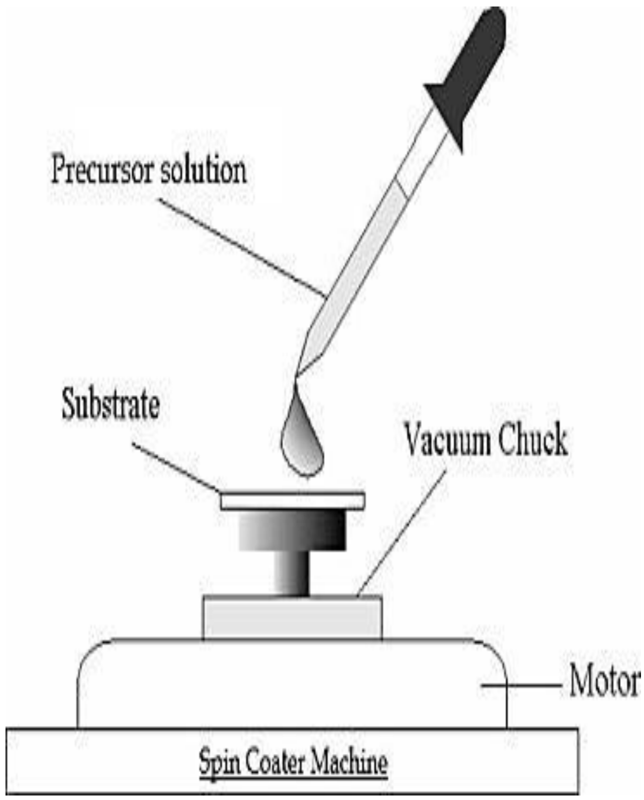


Fig.3.3.1.1 Schematic representation of Spin coating for thin films

3.3.2 Dip Coating

Dip coating is a simple method of depositing uniform thin film onto a substrate, especially small slabs and cylinders. The basic flow is steady, and in it film thickness is set by the viscous force, capillary (surface tension) force and gravity. In this method faster the substrate is withdrawn, the thicker the film is deposited. Therefore, insertion rate of substrate inside the precursor solution is very slow. This can also be overcome by using volatile solutes and combining rapid drying with the basic liquid flow. Fig.3.3.2.1 represents a manual dip coater.

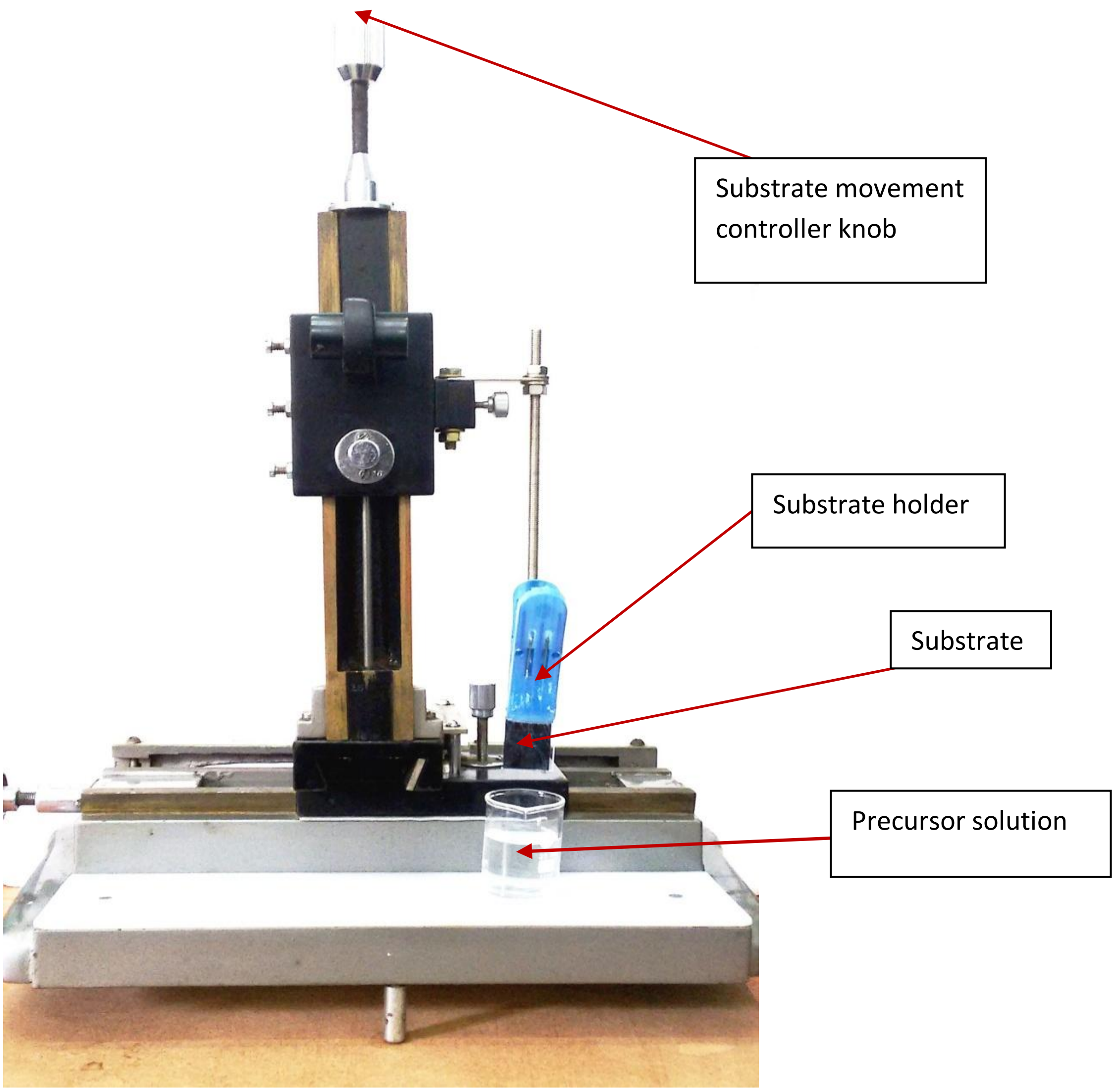


Fig.3.3.2.1 Image of Dip Coating machine

3.3.3 RF Magnetron sputtering

RF co-sputtering technique is used to deposit p-type ZnO thin film using ZnO and Al dual targets in O_2 and N ambient ratio of (60:40). The substrate temperature was fixed at 300 ºC. The deposited p-type thin film is taken out and annealed at 500 °C .After this RF magnetron sputtering is used to depositing n-type ZnO thin by reactive sputtering using Zn as target material and O_2 as reactive gas over the p-type deposited film. Target and substrate (p-ZnO) distance is kept at 10 cm and then the chamber is closed. To remove unwanted gases and moisture, high vacuum of 1.5×10^{-6}mbar is achieved using diffusion pump with rotary pump acting as backing pump. After achieving desired pressure, Ar and O_2 gas is flown inside the chamber by maintaining flow ratio of Ar to O_2 as 2:3. Working pressure in the chamber is kept at 8×10^{-3}mbar. For the intimate bonding between the Zn and O, the substrate surface is kept at temperature 200 ºC. RF power of 150W is applied to the electrodes and film is sputtered for 40 minutes.

CHAPTER 4

4. Result and Discussions

4.1 Structural Characterizations

XRD analyses were done using Rigaku Ultima IV diffractometer, Cu K_{α} radiation of wavelength 0.15418 nm at operating voltage and current 40 kV and 40mA respectively.

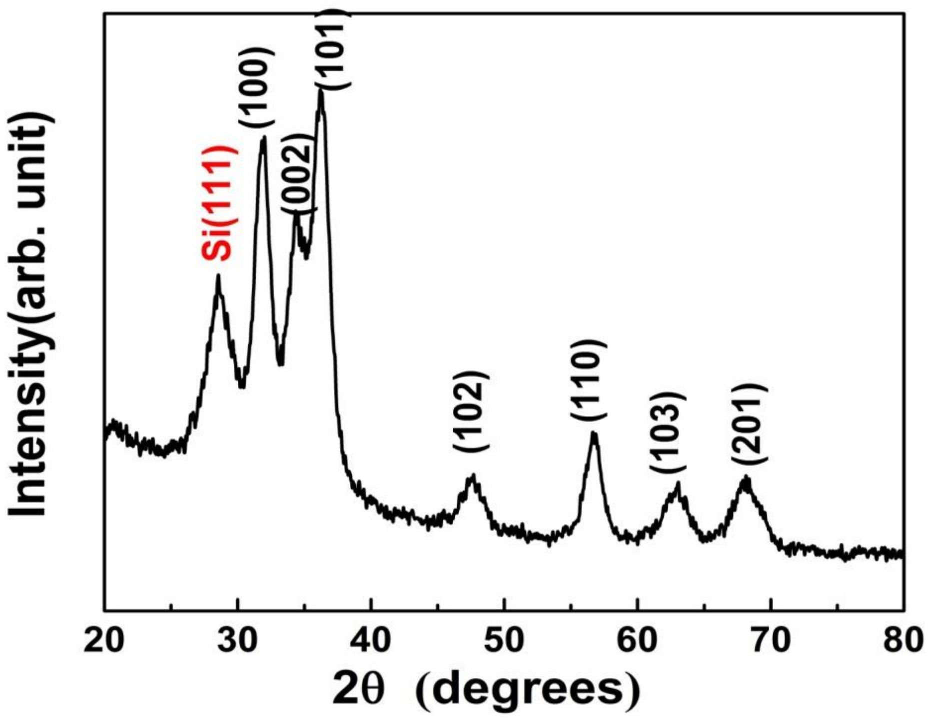


Fig.4.1.1 XRD pattern of p- ZnO thin film dip coated on n-Si and annealed at 300 °C

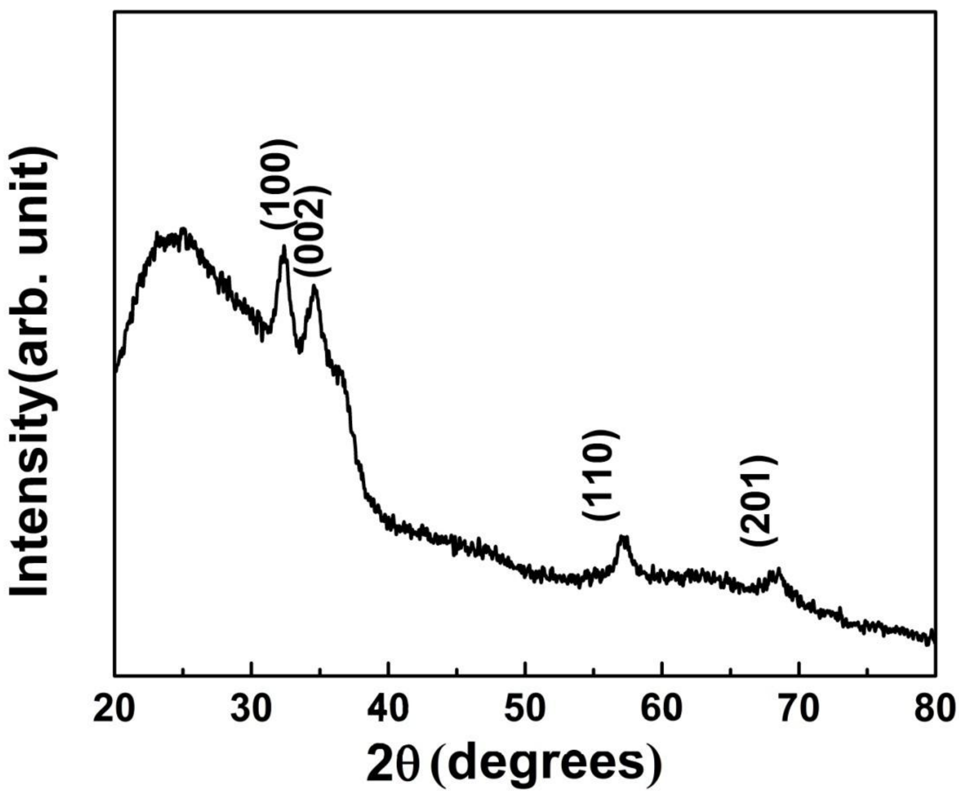


Fig.4.1.2 XRD pattern of p- ZnO thin film dip coated on glass substrate and annealed at 300 °C

The XRD pattern matches well with the corresponding peaks of ZnO thin film representing a polycrystalline nature. **JCPDS Card No. 800074** [Fig.4.1.1]**.** We are also getting a Silicon (111) peak as it is the substrate and also a amorphous peak in Fig.4.1.2 because in that case our substrate is glass [Fig.4.1.2].

4.2 Optical Characterizations

The UV-visible transmittance spectra were taken at room temperature in wavelength range 200-800 nm for calculation of band gap [Fig.4.2].

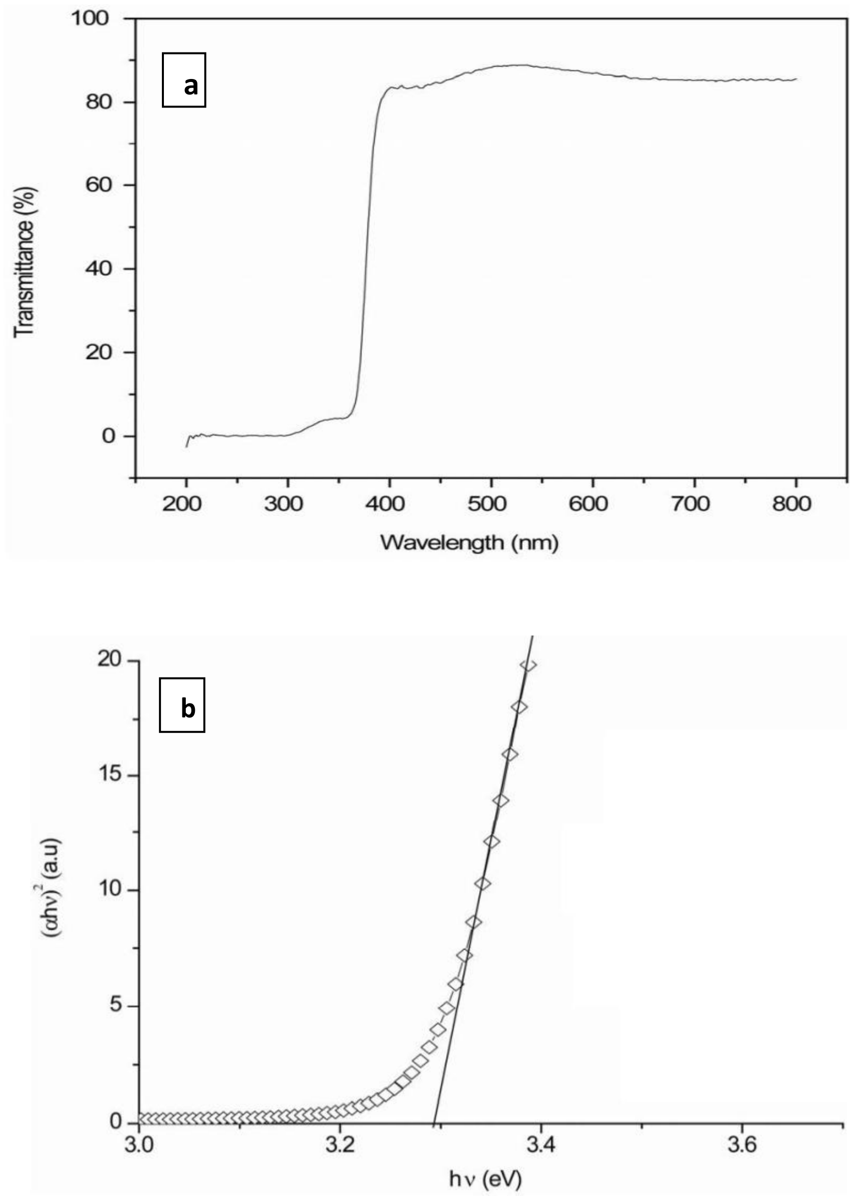


Fig.4.2 (a) Transmission spectrum of undoped ZnO thin film (b) Plot of $(\alpha h\nu)^2$ vs. energy of photon. The band gap of ZnO thin film is found to be 3.29 eV

4.3 I-V Study

I-V characterization of junctions with three different methods and device structures are carried out using KEITHLEY picoammeter/voltmeter source 6487. I-V characteristics are plotted using Origin software.

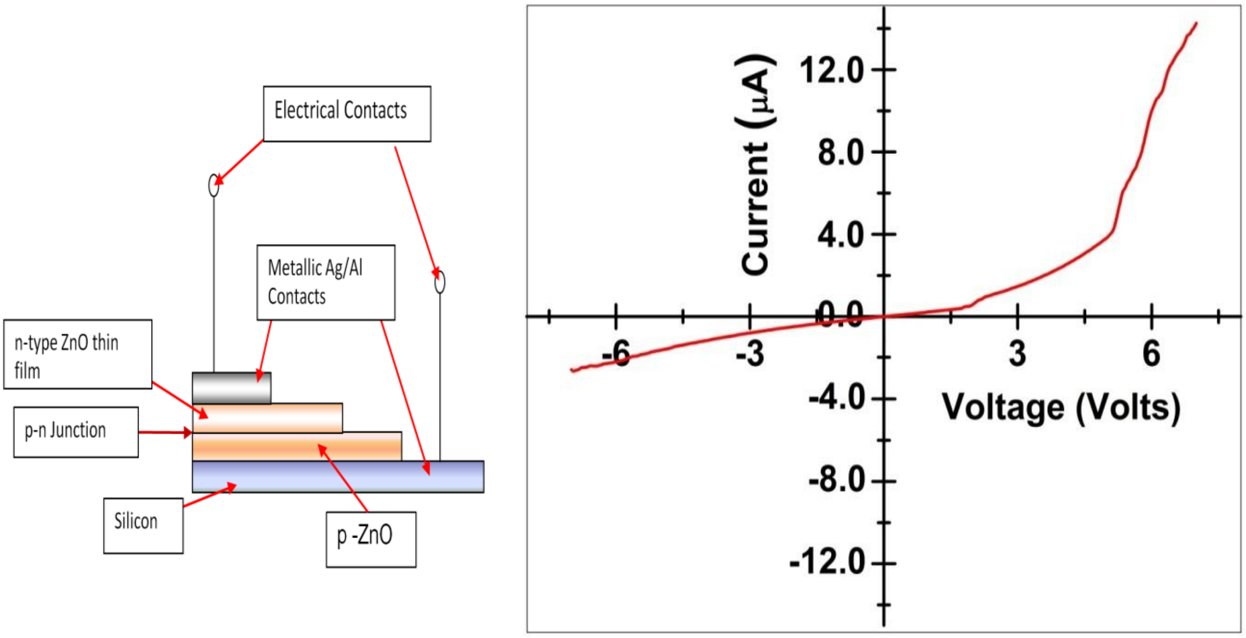


Fig.4.3.1 Junction characterization of n-ZnO (sputtered) on p-ZnO: (Al, N) sputtered

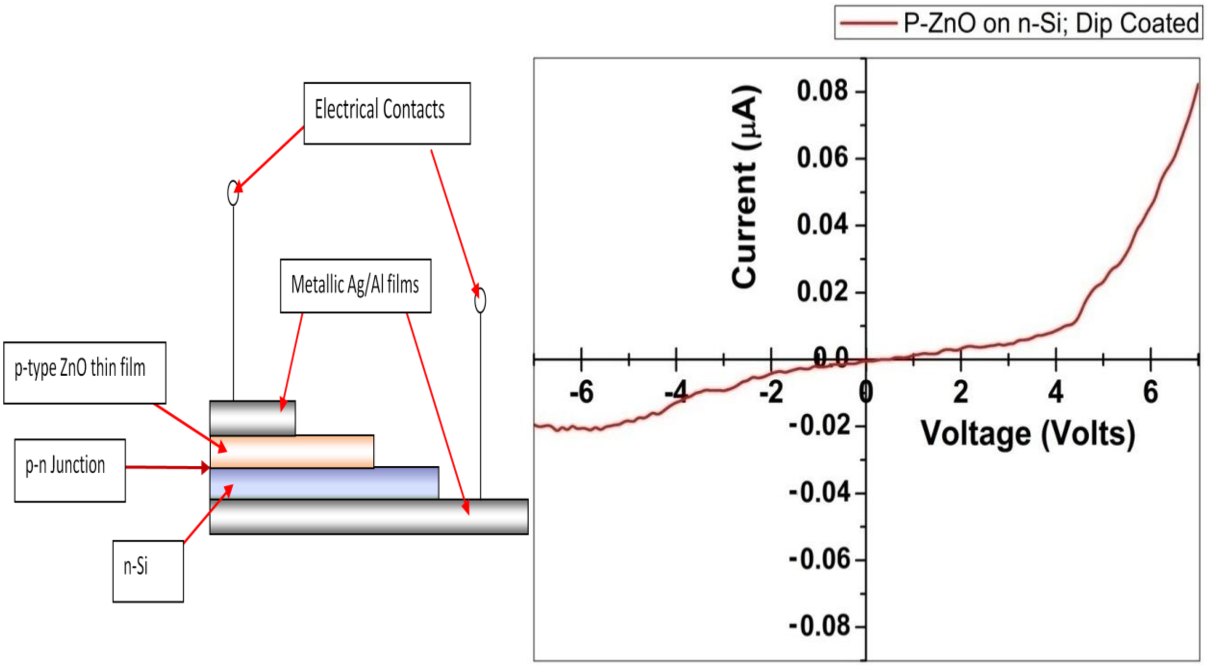


Fig.4.3.2 Junction characterization of p-ZnO on n- Si using dip Coating method

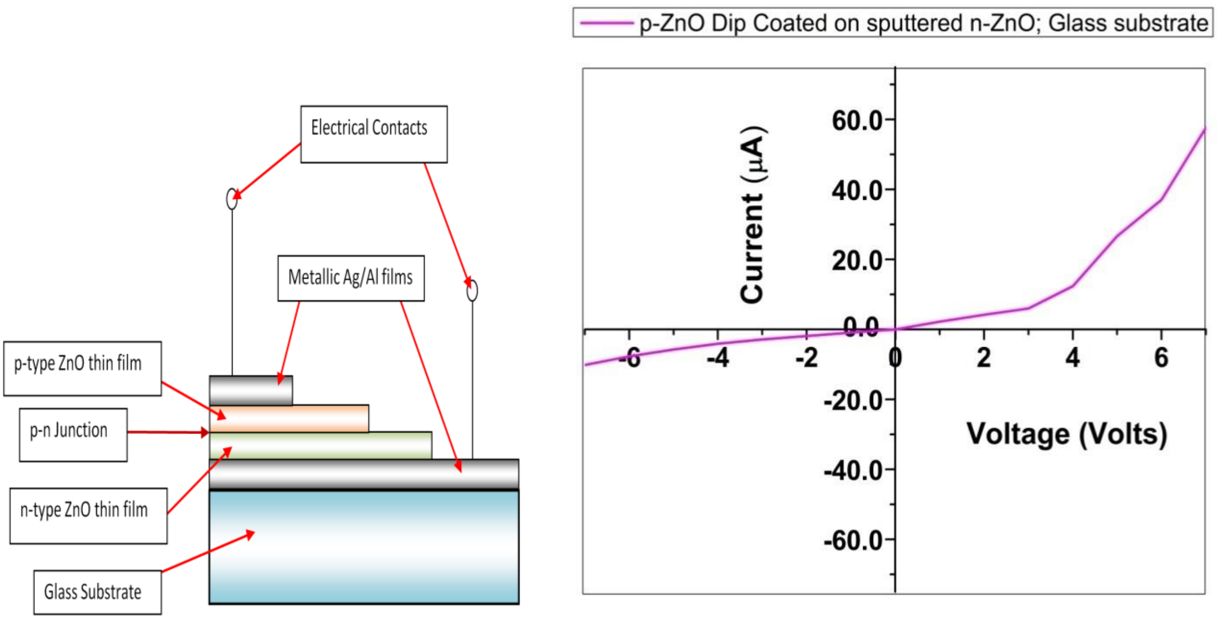


Fig.4.3.3 Junction characterization between p-ZnO (dip coated) and n-ZnO (sputtered); grown on glass substrate

- **Comparison of Junction Performances**

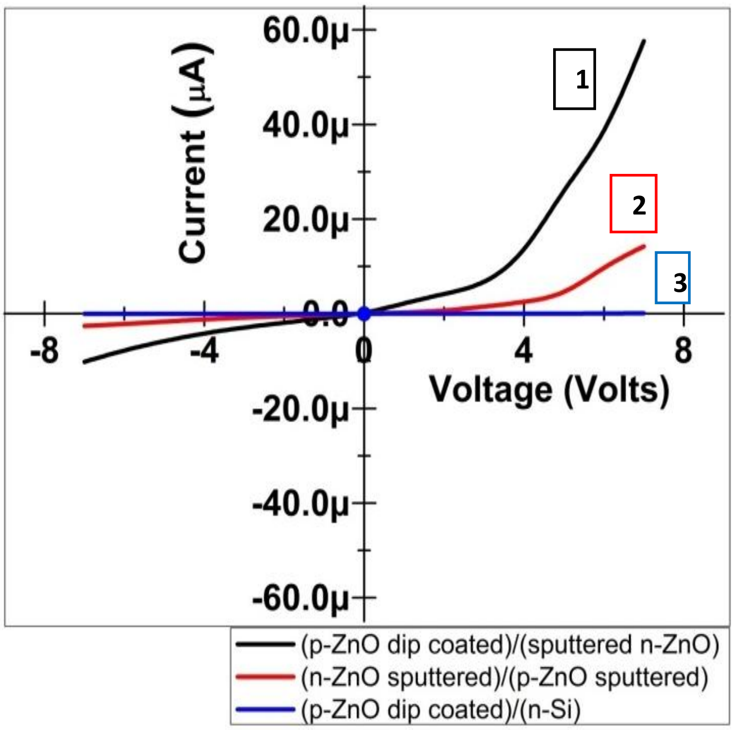


Fig.4.3.4 Comparative study of junction characterizations using three different methods

Fig.4.3.4 gives comparative study of I-V characterization of the following samples:

Sample1. Homo-junction between p-type ZnO dip coated on sputtered n-type ZnO film

Sample2. Homo-junction between p-type ZnO sputtered thin film and sputtered n-type ZnO thin film

Sample3. Hetero-junction between p-type ZnO dip coated thin film and n-type Silicon

From this comparative study it is clear that Sample1 shows high value of current for a particular supplied voltage within the range. In comparison to sample2, sample1 gives better performance due to good interplanar contact formed between films [Fig.4.3.4]. While comparing sample3 with sample1, sample3 has poor junction formed which indicates poor hetero-junction between p-ZnO and n-Silicon.

Conclusion

In this project, p-type and n-type Zinc oxide thin films deposited using different routes on glass and silicon substrates. XRD analysis and UV-visible spectroscopy are carried out for structural confirmation and band gap calculation respectively. Finally, their junction performances were studied by performing I-V measurements using Keithley picoammeter/voltmeter 6487 source unit. The hetero-junction formed between p-ZnO (dip coated) on n-type Si is poor due to lattice mismatch. The junction formed between n-ZnO (sputtered) and p-ZnO (sputtered) thin films has lesser junction performance than sputtered-dip coated thin film junction due to the bombardment of ions during sputtering, which degrades the interface between two types of ZnO semiconductors. The homo-junction between p-ZnO (dip coated) and n-ZnO (sputtered) has shown best junction characteristics, which may be useful for fabrication of electronic devices.

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Nomenclature

E_f	- Fermi energy	DI water	- De ionized water
RTA	- Rapid thermal annealing	GaN	- Gallium Nitride
XRD	- X-ray diffraction	$\triangledown H$	- Formation enthalpy
I-V	- Current- voltage	ZnO: Al	- Aluminium doped Zinc Oxide
V_o	- Oxygen Vacancy	ZnO: (Al, N)	- Dual doped Zinc Oxide (Al, N)
eV	- Electron volts	RF	- Radio Frequency
ZnO	- Zinc Oxide	UV	- Ultraviolet
Si	- Silicon		